

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the Application of

Hirofumi BANDOH et al.

Group Art Unit : 1755

Application No.:10/556,065

Examiner : J. USELDING

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Docket No. : 125721

For : CEMENT DISPERSANT AND CONCRETE COMPOSITION CONTAINING
THE DISPERSANT

DECLARATION UNDER 37 C.F.R. § 1.132

I, Akira IKEDA, a citizen of Japan, hereby declare and state:

1. I have a degree in Science/Chemistry which was conferred upon me by Rikkyo University in Tokyo, Japan in 1996.
2. I have been employed by TOHO CHEMICAL INDUSTRY CO., LTD since 1996 and I have had a total of 12 years of work and research experience in concrete additives and concrete admixture.
3. I am a named co-inventor in the above-captioned patent application.
4. I have a professional relationship with the co-assignee of the above-identified patent application. In the course of that professional relationship, I received compensation directly from the co-assignee for my work relating to research relating to concrete additives and concrete admixture. I am being compensated for my work in connection with this Declaration.
5. I and/or those under my direct supervision and control have conducted the following experiments.

The Declaration evaluates the efficiency of cement dispersant according to the present invention in compounding for ultra high strength concrete (water/cement ratio (hereinafter referred to "W/C ratio"; and water/binder ratio is referred to as "W/B ratio") = 20% or less).

1) Test sample

Compounds A to D and other copolymerizable monomer were compounded in proportions shown in Table I described below, and water-soluble amphoteric copolymers (Example 11 and Comparative Examples 10 to 15) were obtained according to the procedure described below.

<Method for manufacturing copolymer>

Into a glass-made reaction vessel equipped with a stirrer, condensor and three dropping ports, 351 g of water was charged. Nitrogen was introduced in the vessel to make the insider of synthesis system to be nitrogen atmosphere, and the temperature was increased to 80°C. A mixture of 120 g of water, 71.6 g of Compound A (60% solid content), 33.9 g of methacrylic acid (Compound B) (42.6g as metharylic acid Na), 74.7 g of short-chain methoxypolyethylene glycol monomethacrylate (Compound C), 122.5 g of long-chain methoxypolyethylene glycol monomethacrylate (Compound D) and 10.4 g of n-butanol polyethylene glycol methacrylate as other copolymerizable monomer, (when Compound B was assumed to be a Na salt, compounding calculation ratio of Compound A:Compound B:Compound C:Compound D was 15 % by weight:15 % by weight:26 % by weight:44 % by weight, and the compounding calculation ratio of Compounds A to D and other copolymerizable monomers were total amount of Compounds A to D:other copolymerizable monomer = 100 parts by weight:4 parts by weight), and an

aqueous mixed solution of 6.88 g of thioglycolic acid and 72.7 g of water were dripwise added to the synthesis system over 2 hours, and in addition, an aqueous mixed solution of 8.89 g of sodium persulfate and 88.9 g of water was also dropwise added to the synthesis system over 3 hours. Thereafter, maturation and cooling were performed for 2 hours. Subsequently, neutralization was performed using a 48% NaOH aqueous solution until a pH of 7 was obtained, thereby obtaining 991 g (solid content: 31.1 %) of a water-soluble amphoteric copolymer (copolymer of Example 11). This copolymer was a copolymer having a weight average molecular weight of 16,100 which was measured by GPC molecular weight measurement. The measurement conditions are as follows.

Column: Shodex KW-404·4F, 403·4F, 402.5·4F

Eluent: Solution of water:acetonitrile = 50:50 weight ratio and containing 0.5 % of sodium acetate trihydrate and is adjusted to pH6 by acetic acid

Water-soluble amphoteric copolymers (Comparative Examples 10 to 15) were obtained by similar procedures at compounding proportions shown in Table I.

Table I Composition of Example 11 and Comparative Examples 10 to 15 used in comparative tests

	Compound A	Compound B	Compound C	Compound D	Other polymerizable compound	Weight average molecular weight ($\times 10^3$)
Example 11	15	15	26	44	4	16.1
Comparative Example 10	5	15	80	0	4	14.3
Comparative Example 11	5	15	0	80	4	20.5
Comparative Example 12	0	15	32	53	4	18.2
Comparative Example 13	30	15	20	35	4	22.7
Comparative Example 14	5	0	47.5	47.5	4	21.3
Comparative Example 15	5	35	30	30	4	24.8

※ Values of Compounds A to D in the Table I are represented by constitutive parts by weight on a solid content basis

Compounds used in the Comparative tests are as follows:

- Compound A: Compound A-3 (described in Table 1 on page 31 of the present specification)
- Compound B: methacrylic acid
- Compound C: a mixture of 31.1 g of methoxypolyethylene glycol monoacrylate (molecular weight: 250) and 43.6 g of methoxypolyethylene glycol monoacrylate (molecular weight: 1000) (weight ratio = 42%:58%)
- Compound D: a mixture of 81.0 g of methoxypolyethylene glycol monoacrylate (molecular weight: 2000) and 41.5 g of methoxypolyethylene glycol monoacrylate (molecular weight: 4000) (weight ratio = 66%:34%)
- Other copolymerizable compound: n-butanol polyethylene glycol methacrylate (number of additive molecule of polycryl glycol: 3)

※ Example of compounding calculation ratio in Example 11

Compound A: 71.6 g (solid content: $71.6 \text{ g} \times 0.6 = 43\text{g}$)

Compound B: 33.9 g (solid content (as sodium salt): 108 (Na methacrylate molecular weight) $\times 33.9 \text{ g}/86$ (methacrylic acid molecular weight)) = 42.6 g)

Compound C (total weight): 74.7 g (100 % of solid content)

Compound D (total weight): 122.5 g (100 % of solid content)

Compound A:Compound B:Compound C:Compound D = 43:42.6:74.7:122.5
(solid content) = 15 % by weight:15 % by weight:26 % by weight:44 % by weight

Total weight of Compounds A to D:other compolymerizable compound =
282.8:10.4 = 100 parts by weight:4 parts by weight

2) Test method and result of test

2-1) Comparative Test Example 1: Mortar flow test (W/B ratio = 12 %)

Samples were prepared according to the processes of Test Example 1 of the present specification (paragraphs [0070] and [0071]) and mortar flow test was carried out.

In details, 110.5 g of sand (silica sand No. 4; density being 2.60 g/cm³), 619.5 g of silica fume cement (density being 3.08 g/ cm³), 32.5 g silica fume and 15.0 g of expanding agent (ettringite-type) were weighed, and mixed by a hyper mortar mixer (manufactured by Kabushiki Kaisha Marutoh Seisakusho) for 30 seconds. Next, 69.7 g (solid content: 21.4 g, total of solid content basis : binder (silica fume cement, silica fume, expanding agent) being 3.5 %)) of copolymer of the respective Example 11 and Comparative Examples 10 to 15 and 80 g of water were added (W/B ratio = 12 %, sand/binder ratio = 16.6 %) and kneaded at low speed for 180 seconds to prepare mortal paste.

The mortar thus prepared was poured into a hollow cylindrical container and charged up to the top end of the container, the container having ϕ 50 mm x H50 mm. Immediately after charging, the hollow cylindrical container was lifted up at a predetermined rate in a direction perpendicular to an acrylic resin-made plate. After one minute and three minutes from the starting of lifting up the hollow cylindrical container, the maximum diameter of spread of the mortar and the diameter perpendicular thereto were measured, and the average was obtained from the two diameters thus measured. The obtained result was shown in Table II.

Table II Result of mortal flow test

Copolymer	Mortar flow value (mm)	
	After one minute	After three minutes
Example 11	116	128
Comparative Example 10	89	96
Comparative Example 11	83	84
Comparative Example 12	102	107
Comparative Example 13	71	76
Comparative Example 14	Mortar was not formed.	Mortar was not formed.
Comparative Example 15	64	67

As shown in Table II, in the result of mortar test according to mortar formulation for ultra high strength concrete (W/B ratio = 12 %), the results that the copolymers of Comparative Example 10 and Comparative Example 11 which only contained either of Compound C or Compound D show such a result that fluidity

was low in comparison with the results of using the copolymer of Example 11.

Moreover, the result of copolymer of Comparative Example 12 in which the copolymerizing proportion of Compound A was 0 is such a result that it lacked fluidity in comparison with the result of Example 11 and the spread of flow after 3 minutes was not observed so much. The result of copolymer of Comparative Example 13 which contains copolymerizing proportion of Compound A much more than the prescribed range (5 to 25 % by weight) was also such a result that it lacked fluidiy.

Still moreover, copolymer of Comparative Example 14 in which copolymerizing proportion of Compound B was 0 showed such a result that mortar was not prepared at all. Reversely, the result of copolymer of Comparative Example 15 in which copolymerizing proportion of Compound B contains much more the prescriberd range (5 to 30 % by weight) was such a result that fluidiy was remarkably inferior.

2-2) Comparative Test Example 2: Mortar flow test (W/B ratio = 20 %)

Samples were prepared according to the procedure of Test Example 1 of the present spcification (the paragraphs [0070] and [0071]) and mortar flow test was carried out.

In details, 396 g of sand (crushed sand No. 4; density being 2.64 g/cm³) and 403 g of silica fume cement (density being 3.08 g/ cm³) were weighed, and mixed by a hyper mortar mixer (manufactured by Kabushiki Kaisha Marutoh Seisakusho) for 30 seconds. Next, 5.0 g (solid content: 2.0 g, total of solid content basis:binder: 0.5 %) of copolymer of the respective Examples 3 to 5 (described in Table 2 on page 33 of the present specification) and Comparative Examples 10 to 15 and 75.6 g of

water were added (W/B ratio = 20 %, sand/binder ratio = 98.3 %) and kneaded at low speed for 180 seconds to prepare mortal paste.

The mortar thus prepared was poured into a hollow cylindrical container and charged up to the top end of the container, the container having ϕ 50 mm x H50 mm. Immediately after charging, the hollow cylindrical container was lifted up at a predetermined rate in a direction perpendicular to an acrylic resin-made plate. After the mortar stopped spreading and completely stood still, the maximum diameter of spread of the mortar and the diameter perpendicular thereto were measured, and average value was obtained from the two diameters thus measured. These operations were carried out immediately after the formation of mortar paste and after 30 mintues after the preparation. The obtained result was shown in Table III.

Table III Result of mortar flow test

Copolymer	Mortar flow value (mm)	
	Immediately after	After 30 minutes
Example 3	185	180
Example 4	186	182
Example 5	180	181
Comparative Example 10	158	140
Comparative Example 11	180	165
Comparative Example 12	182	170
Comparative Example 13	113	91
Comparative Example 14	Mortar was not formed.	Mortar was not formed.
Comparative Example 15	120	63

As shown in Table III, in the result of mortar test by mortar formation for ultra high strength concrete (W/C = 20 %), the result that copolymers of the Comparative Examples 10 and 11 which contained only either one of Compound C or Compound D was a result that they were inferior in water reducing property, especially, slump flow retention (maintainability) in comparison with the results that the copolymers of Examples 3 to 5 were used.

Moreover, the result of the copolymer of Comparative Example 12 in which copolymer proportion of Compound A was 0 was almost same result with the result of Examples 3 to 5 with respect to water reducing property, but it lacked maintainability.

The result of the copolymer of Comparative Example 13 in which the copolymer proportion of Compound A contained much more than the prescribed range (5 to 25 % by weight) showed such a result that water reducing property was remarkably inferior.

Still moreover, the copolymer of Comparative Example 14 in which copolymer proportion of Compound B was 0 did not form mortar, and result of using the copolymer of Comparative Example 15 which was out of the prescribed range (5 to 30 % by weight) in the copolymer proportion of Compound B was such a result that it was remarkably inferior in water reducing property.

2-3) Comparative Test Example 3: Concrete test

By taking the result of mortar flow test in the item 2-1) described above into account, evaluation as a cement dispersant (water reducing agent) for ultra high strength concrete was carried out in concrete test at the concrete formation described in the below-mentioned Table IV by using compolymers of Example 11,

Comparative Example 10 and Comparative Example 12.

A 55 liters forced twin-screw mixer was used for kneading concrete. After a binder (cement), a fine aggregate and an expanding agent were previously kneaded for 15 seconds, the copolymers of Example 11, Comparative Examples 10 and 12 and water were placed in and kneaded for 240 seconds. Thereafter, coarse aggregate was placed in and kneaded for 330 seconds and excluded to carry out fresh concrete test (slump test: JIS A 1101 (measurement of spread of fresh concrete as flow value). Then, as index of concrete viscosity, fresh concrete was charged into a cylindrical frame and thus charged frame was placed in water of 42 °C as it was. After predetermine time passed, the frame was taken off. After taking off the frame, vapour cure for 90°C x one week was carried out and compression strength was measured. The obtained result is shown in Table V.

Table IV Concrete

W/B (%)	s/a (%)	Unit amount (kg/m ³)					
		water	binder	fine aggregates	coarse aggregates	expanding agent	PP fiber
12	24. 3	160	1304	221	802	30	1

Binder: silica fume cement (density: 3.08 g/cm³)

Fine aggregates: sand (density: 2.64 g/cm³)

Coarse aggregates: hard crushed stone (density: 2.65 g/cm³)

Expanding agent: ettringite-type expanding agent

PP fiber: PP fiber for ultra high strength concrete on the market was used.

s/a: rate of fine aggregates

Table V Result of concrete test

Copolymer	Addition amount ^{*1} (%)	Slump flow value (mm × m) m)	Time that flow stopped	Air amount ^{*2} (%)	Compression strength (N/mm ²)
Example 11	3. 5	690×685	178 seconds	2. 6	177
Comparative Example 10	3. 5	520×505	133 seconds	2. 8	170
Comparative Example 12	3. 5	480×465	121 seconds	3. 6	164

- * 1: Water was added so as to adjust concentration of solid content to become 30 %, which was added as a part of water to a binder (binder + expanding agent) at proportion of 3.5 % uniformly as solid content amount of copolymer
- * 2: Air was designed to become 2 %.

Fresh concrete for ultra high strength was extremely low in water:powder or binder ratio (W/B ratio) and thus, required high load at kneading, but had low state of yield value, so-called dilantancy behaviour. For this reason, high load was applied at kneading time in manufacturing concrete, but the fresh concrete was slowly flowed immediately after it was poured into a flow cone and taken off therefrom and slump began to be spreaded.

Result that the copolymer of Example 11 was used showed very excellent fluidity in a concrete composition compounded for ultra high strength concrete of W/B = 12 %.

On the other hand, the copolymer of Comparative Example 10 in which only short-polyalkylene glycol momomer (Compound C) was used or the copolymer of

Comparative Example 12 in which Compound A was not used showed results that they were inferior in fluidity of slump flow. Moreover, result of using the copolymer of Comparative Example 12 showed a result that air amount was increased and compression strength was lowered.

Reason that great differences of slump flow were generated is assumed to be reside in a point that the present test for fresh concrete was conducted under high viscosity peculiar to ultra high strength concrete, i.e., slump flow value is determined not only on water reducing property of a dispansant (water reducing agent), but also by synergistic effect with viscosity of paste itself.

The result of flow stopping time (time until flowing fresh concrete was completely stopped) was such a result that the concrete prepared by using the copolymer of Example 11 flowed very slowly in comparison with the copolymers of Comparative Examples. When both results that the copolymers of Comparative Examples 10 and 12 were used are compared, it was resulted in that the concrete using the copolymer of Comparative Example 10 containing Compound A showed that the concrete flowed longer than that of Comparative Example 12.

Namely, from these results, the incorporation of Compound A into copolymer at suitable amount contributes decrease of concrete viscosity.

6. I hereby declare that all statements made herein of my own knowledge are true, and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine and/or imprisonment under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing therefrom.

Date: Feb. 05. 2009 Akira Ikeda

Akira Ikeda